

Tutorial 5

(1) Surface structure to workfunction

(2) Chemical shifts in core levels: Surface example

(3) Chemical shifts in core levels: Molecular example

Using periodic DFT calculations
to relate surface structure
to basic, measurable quantities

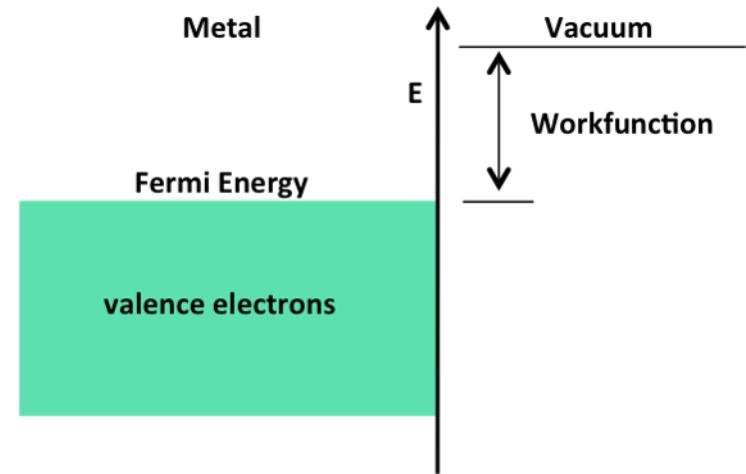
Au(111):CO – Workfunction Changes

Basic workflow:

Step 1: Bulk Au lattice parameter

**Step 2: Relaxed, ideal Au(111) surface:
Structure and workfunction**

**Step 3: 1ML of CO on Au(111) a-top site:
Structure and workfunction**



Functional choice: PBE

**Initial estimate for cutoffs: 300 eV based on ENMIN for C and O from
POTCAR for PAW_PBE**

Tutorials: File System – Surface/Interface

/software/Workshop14/Tutorials/Tutorial5

Au111CO

1_1_AuBulk

1_2_Au7ML1x1

1_3_Au7ML1x1CO

1_4_1x1CO

CoreInit

CoreInit

CoreInit

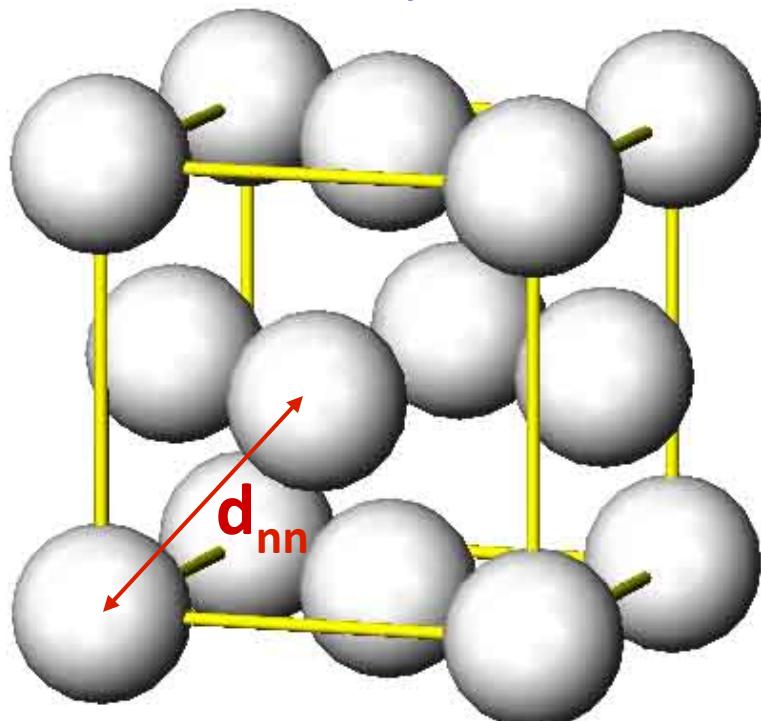
To run core levels in lower directories:

```
> cp CONTCAR CoreInit/POSCAR  
> cp CHGCAR CoreInit/.  
> cp WAVECAR CoreInit/.
```

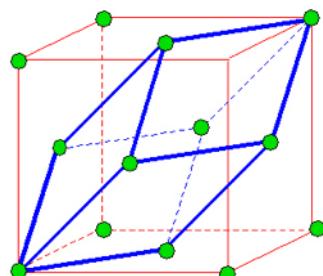
Script for job submission: vpbs.com

Au fcc Structure & (111) Surface

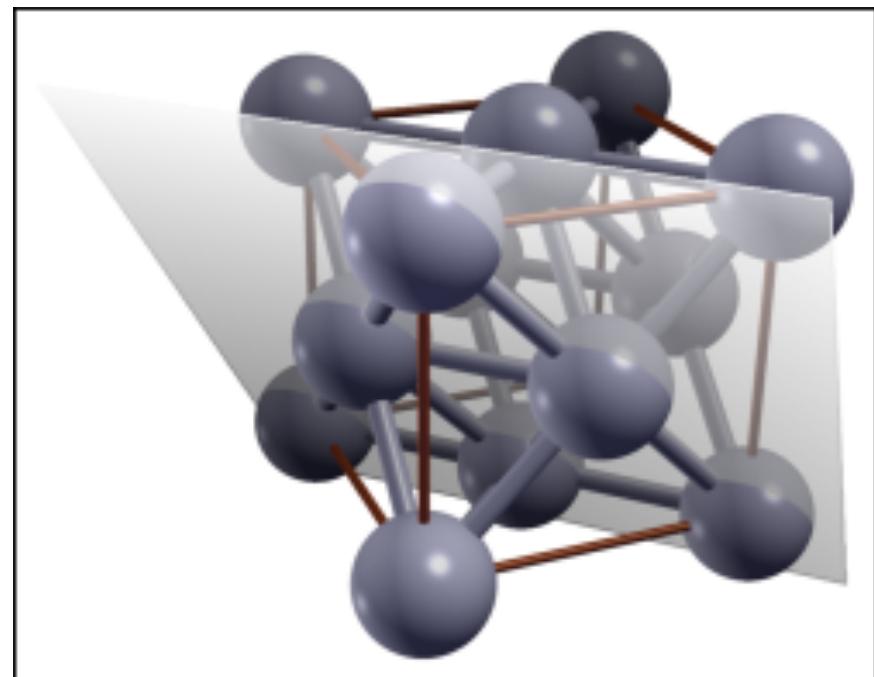
fcc structure
4 atoms / cube



Standard
1 atom cell



Cut for the (111) surface



Bulk Au fcc Lattice Parameter

Key Input Choices

INCAR

```
Electronic Relaxation 1
  PREC = accurate
  ENMAX = 400.00 eV
```

30%-40% larger to support volume changes

```
Ionic Relaxation
```

```
  NSW = 10
```

```
  IBRION = 2  ionic relax: 0-MD 1-quasi-New 2-CG
```

```
  ISIF = 3  stress and relaxation of cell size / shape
```

Optimize volume of the cell by minimizing stress

```
DOS related values:
```

```
  ISMEAR = 1  Meth-Pax
```

```
  SIGMA = 0.2
```

KPOINTS

```
Automatic mesh
```

```
0
```

```
Gamma
```

```
  9  9  9
```

```
  0.  0.  0.
```

K-point sample / smearing linked
Should be tested empirically

Optimized Au fcc Bulk Lattice Parameter: PBE

Key Output

| | | | | | | |
|---------------------|----------|----------|-----------------|---------|---------|---------|
| Total | -0.00916 | -0.00916 | -0.00916 | 0.00000 | 0.00000 | 0.00000 |
| in kB | -0.81000 | -0.81000 | -0.81000 | 0.00000 | 0.00000 | 0.00000 |
| external pressure = | | -0.81 kB | Pullay stress = | | 0.00 kB | |

VOLUME and BASIS-vectors are now :

energy-cutoff : 400.00

volume of cell : 18.13

direct lattice vectors

| | | |
|-------------|-------------|-------------|
| 0.000000000 | 2.084990742 | 2.084990742 |
| 2.084990742 | 0.000000000 | 2.084990742 |
| 2.084990742 | 2.084990742 | 0.000000000 |

reciprocal lattice vectors

| | | |
|--------------|--------------|--------------|
| -0.239809218 | 0.239809218 | 0.239809218 |
| 0.239809218 | -0.239809218 | 0.239809218 |
| 0.239809218 | 0.239809218 | -0.239809218 |

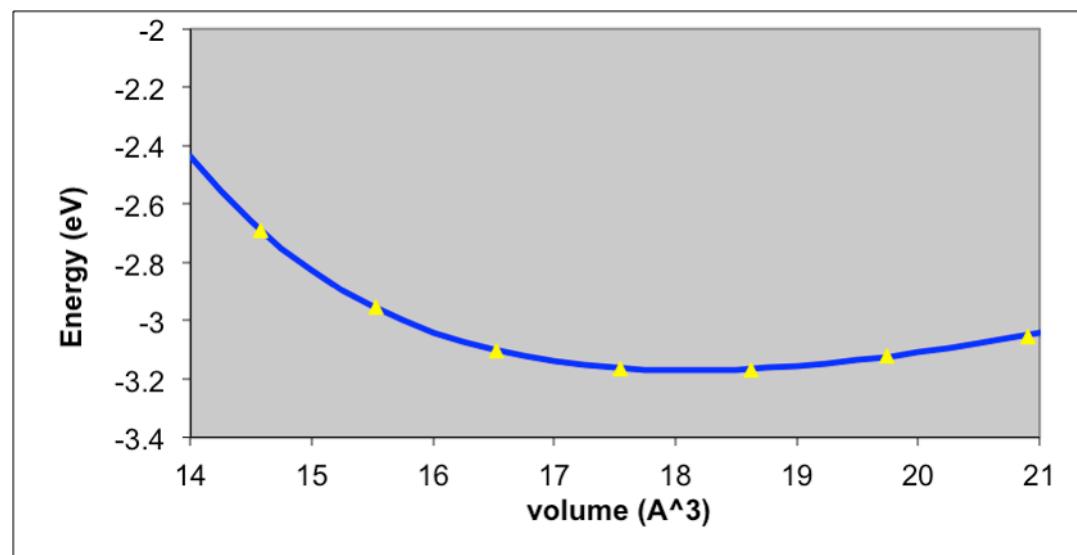
length of vectors

| | | |
|-------------|-------------|-------------|
| 2.948622185 | 2.948622185 | 2.948622185 |
|-------------|-------------|-------------|

| | | |
|-------------|-------------|-------------|
| 0.415361750 | 0.415361750 | 0.415361750 |
|-------------|-------------|-------------|

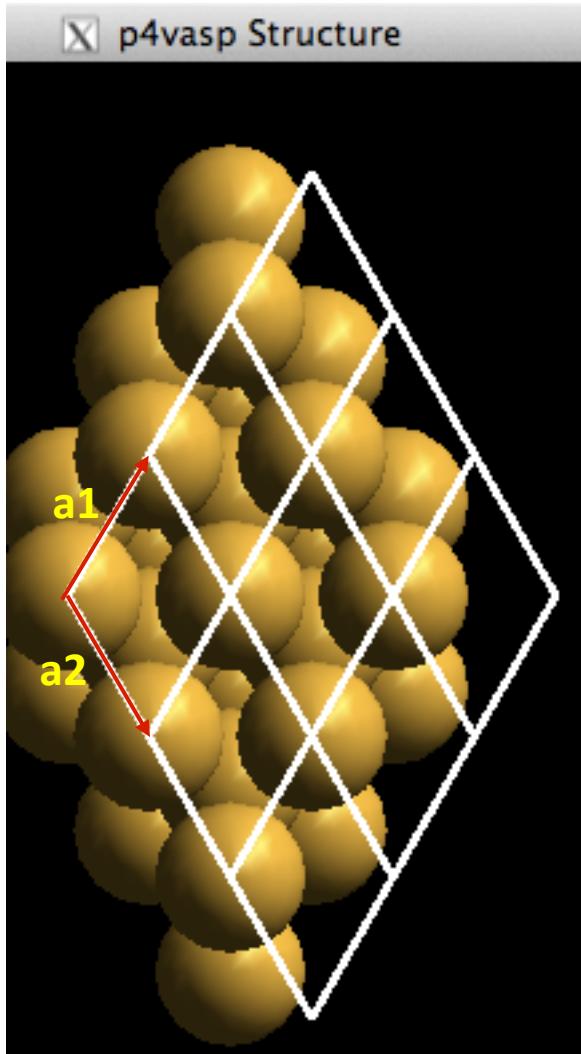
Predicted
lattice
parameter
 $a = 4.165 \text{ \AA}$
(exp 4.08 \AA)

Very close to fit
of discrete $E(V)$
data to an
equation of state
(Murnaghan)
 $a = 4.168 \text{ \AA}$



Ideal Surface Set-up

1x1 surface cell
(3 x 3 cells visualized)



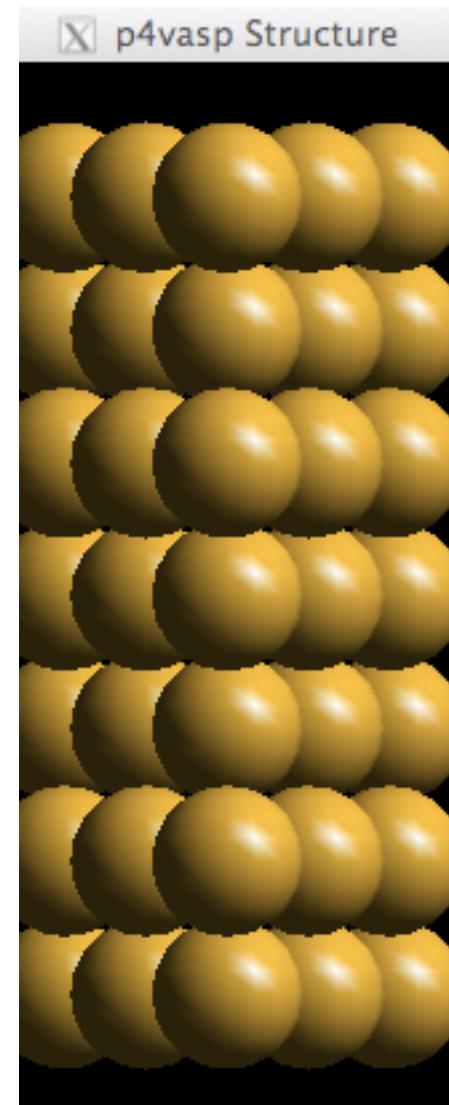
Surface Lattice

$$\begin{aligned} \mathbf{a}_1 &= \left(\frac{1}{2}d_{nn}, \frac{\sqrt{3}}{2}d_{nn}, 0 \right) \\ \mathbf{a}_2 &= \left(\frac{1}{2}d_{nn}, -\frac{\sqrt{3}}{2}d_{nn}, 0 \right) \end{aligned}$$

Layer spacing

$$d_{layer} = \sqrt{\frac{2}{3}}d_{nn}$$

7 monolayer slab



Ideal Surface Calculation

POSCAR

```
Au(111) 7ML1x1 12 ML cell -- PBE
1.00000000000000
1.4743000000000001 -2.5535625055987967 0.0000000000000000
1.4743000000000001 2.5535625055987967 0.0000000000000000
0.0000000000000000 0.0000000000000000 28.8903000000000000
Au
7
Selective dynamics
Direct
0.00000000000000 0.00000000000000 -0.25000000000000 T T T
0.333333333333357 0.6666666666666643 -0.1666666666666667 T T T
0.6666666666666643 0.333333333333357 -0.0833333333333333 F F F
0.00000000000000 0.00000000000000 0.00000000000000 F F F
0.333333333333357 0.6666666666666643 0.0833333333333333 F F F
0.6666666666666643 0.333333333333357 0.1666666666666667 T T T
0.00000000000000 0.00000000000000 0.25000000000000 T T T
-
Fix middle layers for bulk-like region
```

Choose 12 ML ideal total (with vacuum)

Ideal Surface Calculation

INCAR

```
Electronic Relaxation 1
  PREC = accurate
  ENMAX = 300.00 eV
  NELM = 35;      Surface calculations can be slower to converge
  NELMIN = 5
  EDIFF = 1E-05  stopping-criterion for ELM

  Ionic Relaxation
    NSW = 10      Relax internal coordinates to F-max = 0.05 eV/A
    IBRION = 2     ionic relax: 0-MD 1-quasi-New 2-CG
    ISIF = 0       no stress and relaxation of cell size / shape
    ISYM = 2       symmetry on
    IWAVPR = 1     prediction: 0-non 1-charg 2-wave 3-comb
    LCORR = T      Harris-correction to forces
    EDIFFG = -0.050 Force criterion for stopping ionic relaxation

  DOS related values:
    ISMEAR = 1     Meth-Pax Match bulk: but note 2D mesh
    SIGMA = 0.2

  Electronic Relaxation 2
    ALGO = Fast    algorithm: Davidson --> RMM
    LDIAG = T      sub-space diagonalisation
    LREAL = A      R-space projection
    LPLANE = T     minimize FFT communication -- parallel
    NSIM = 4       blocking for RMM-DIIS algorithm
    NPAR = 4       Argument for parallel organization

  Number of bands   7 au atoms / cell → 77 electrons
  NBANDS = 48      require > 38 bands

  Output flags
  LVHAR = T       Output local potential Need reference electrostatic potential
```

KPOINTS

```
Automatic mesh
0
Gamma
  9  9  1
  0.  0.  0.
^-
```

Parallel Computation

Script Header (vpbs.com)

```
#!/bin/sh
#PBS -l nodes=1:ppn=8,walltime=1:00:00
#PBS -q cfn_workshop      1 node w/ 8 cores per node
#PBS -N au7ml1x1
#PBS -j oe
#PBS -V
```

INCAR

```
Electronic Relaxation 2
ALGO    =   Fast      algorithm: Davidson --> RMM
LDIAG   =     T      sub-space diagonalisation
LREAL   =     A      R-space projection
LPLANE  =     T      minimize FFT communication -- parallel
NSIM    =     4      blocking for RMM-DIIS algorithm
NPAR    =     4      Argument for parallel organization
```

NPAR controls internal data structure & how data multiple cores are utilized.
Rule of thumb – approximately sqrt of number of cores and divisible into NBANDS

Au(111):1x1 Surface Output

OUTCAR: Final positions & forces

| POSITION | | | TOTAL-FORCE (eV/Angst) | | |
|----------|----------|----------|------------------------|----------|-----------|
| 0.00000 | 0.00000 | 21.65499 | 0.000000 | 0.000000 | -0.015221 |
| 1.47430 | 0.85119 | 24.08845 | 0.000000 | 0.000000 | -0.029450 |
| 1.47430 | -0.85119 | 26.48277 | 0.000000 | 0.000000 | -0.001820 |
| 0.00000 | 0.00000 | 0.00000 | 0.000000 | 0.000000 | 0.000000 |
| 1.47430 | 0.85119 | 2.40753 | 0.000000 | 0.000000 | 0.001820 |
| 1.47430 | -0.85119 | 4.80185 | 0.000000 | 0.000000 | 0.029450 |
| 0.00000 | 0.00000 | 7.23531 | 0.000000 | 0.000000 | 0.015221 |

Outer layer spacing > bulk:

2.433 vs 2.408 Å

< F-max

average (electrostatic) potential at core
the test charge radii are 1.2098
(the norm of the test charge is
1.0000)
1 -49.9214 2 -50.2595 3 -50.3653 4 -50.3627 5 -50.3653
6 -50.2595 7 -49.9214

Proxy for core levels: Surface different

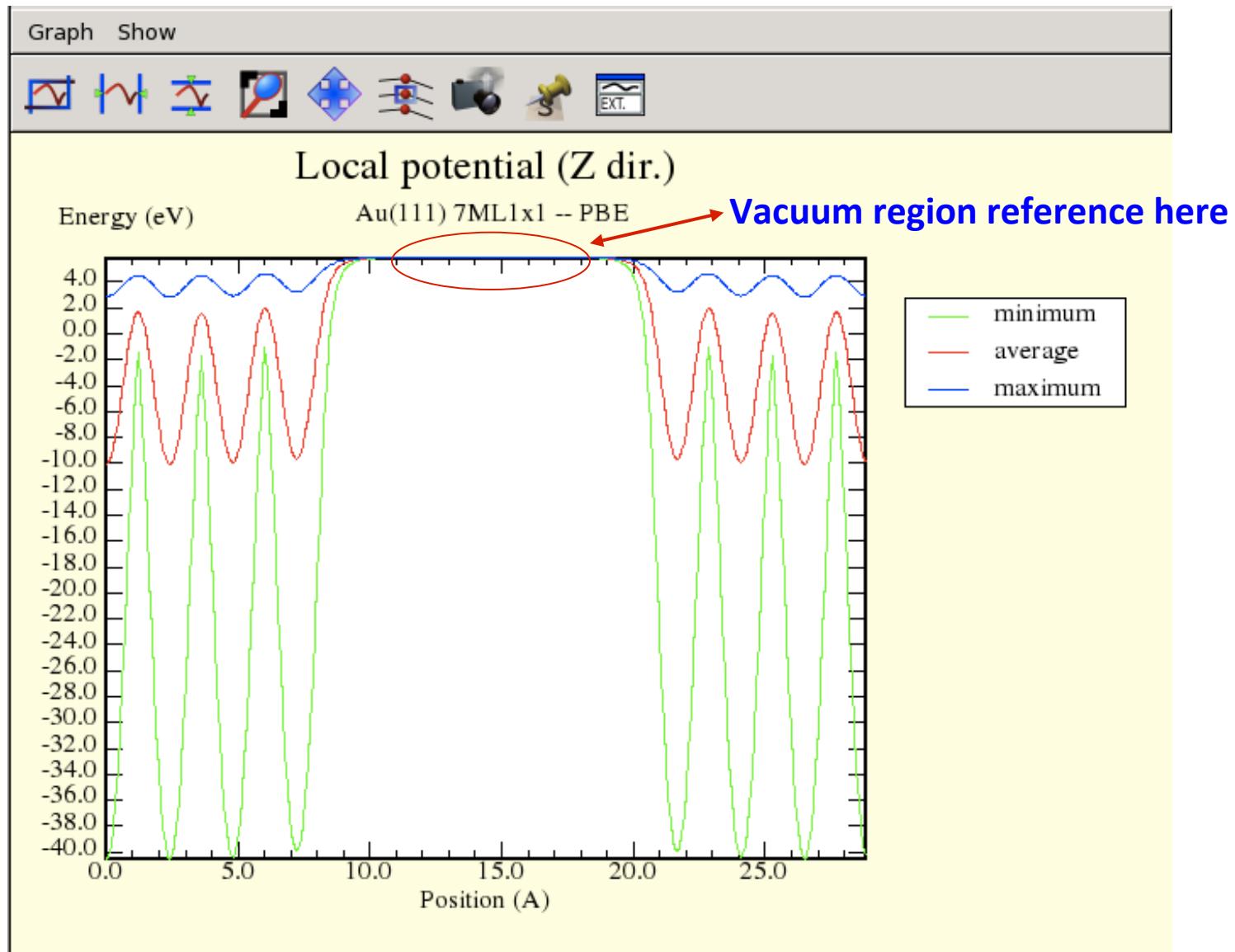
E-**fermi** : 0.6478 XC(G=0): -7.7481 alpha+bet : -5.5845

Fermi energy → workfunction, but what is the reference vacuum?

| k-point | 1 : | 0.0000 | 0.0000 | 0.0000 |
|----------|---------------|------------|--------|--------|
| band No. | band energies | occupation | | |
| 1 | -8.3255 | 2.00000 | | |
| 2 | -7.8326 | 2.00000 | | |

Au(111):1x1 Average Potential & Vacuum

P4Vasp: Electronic / Local Potential



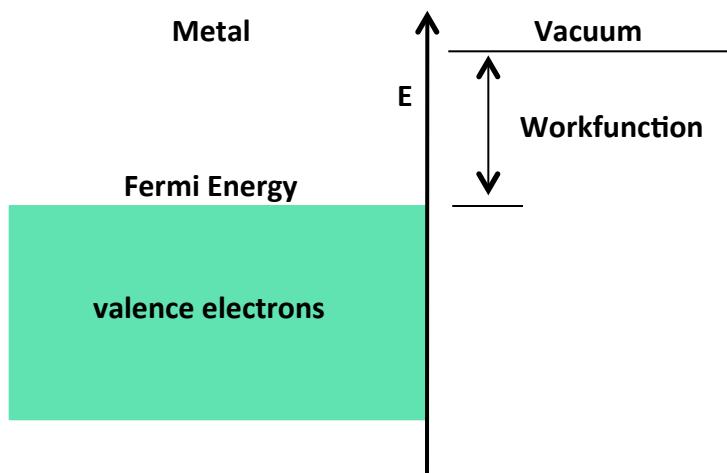
Au(111):1x1 Workfunction

Reference potential from P4Vasp data export,
mid-point of vacuum: 5.851 eV

Fermi energy from OUTCAR: 0.648 eV

Calculated Workfunction: 5.2 eV

(Expt: 5.1 – 5.5 depending on facet)



Au(111):1x1:CO Setup

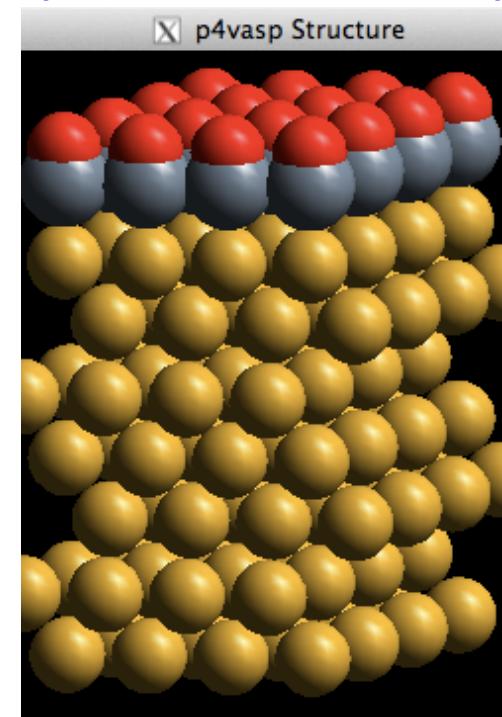
POSCAR:

Add C & O to one side only
Freeze other side ideal

```
Au   C   0
    7   1   1
Selective dynamics
Direct
 0.000000000000000  0.000000000000000 -0.250000000000000 F   F   F
 0.333333333333357  0.666666666666643 -0.166666666666667 F   F   F
 0.666666666666643  0.333333333333357 -0.083333333333333 F   F   F
 0.000000000000000  0.000000000000000  0.000000000000000 F   F   F
 0.333333333333357  0.666666666666643  0.083333333333333 F   F   F
 0.666666666666643  0.333333333333357  0.166666666666667 T   T   T
 0.000000000000000  0.000000000000000  0.250000000000000 T   T   T
 0.000000000000000  0.000000000000000  0.351000000000000 T   T   T
 0.000000000000000  0.000000000000000  0.392000000000000 T   T   T
```

Nota Bene: Best to start with accurate C-O bond length (1.24 Å)

1x1 surface cell
with CO a-top
(4 x 4 cells visualized)

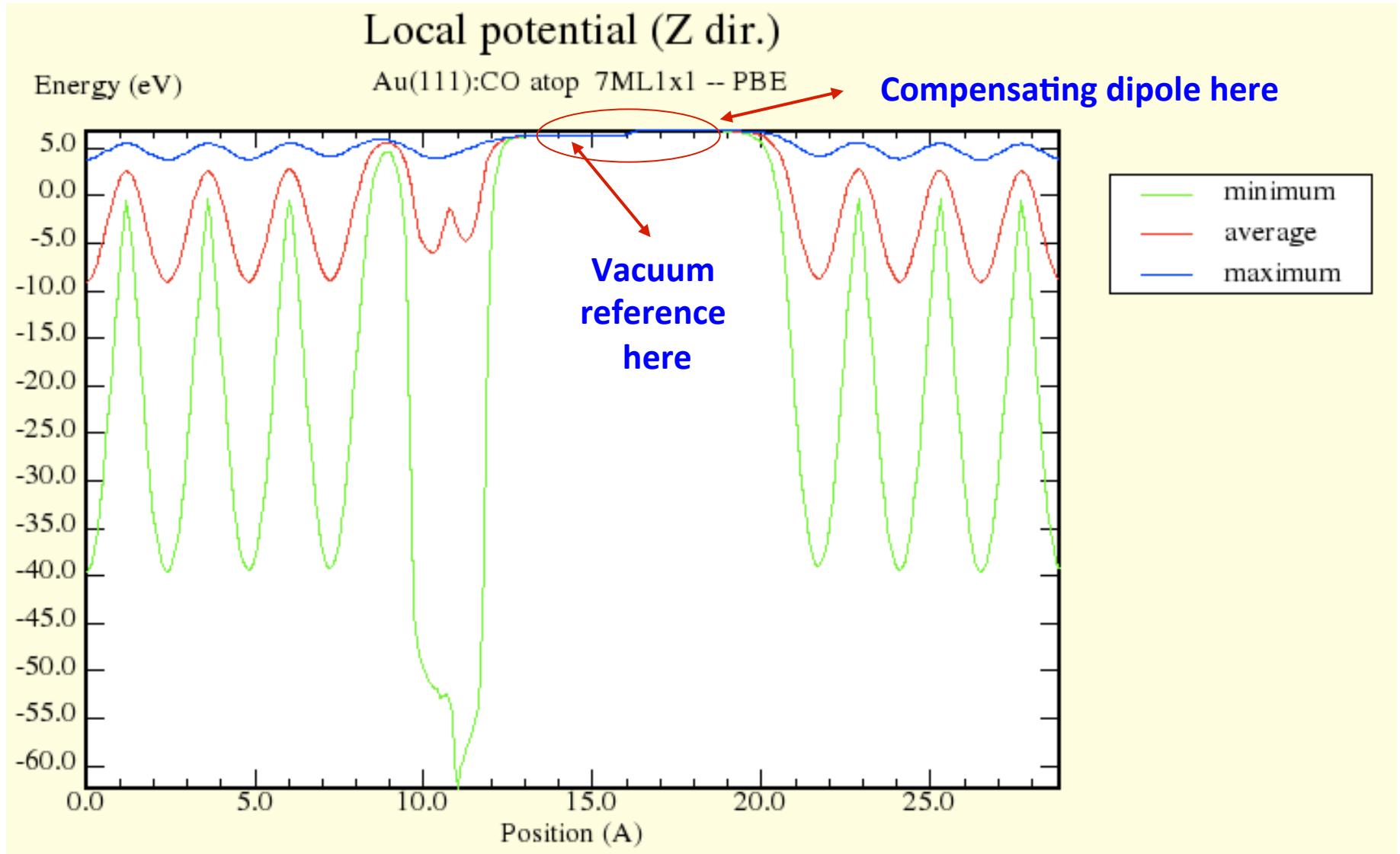


INCAR:

Need to compensate for net dipole

Dipole correction, z-axis, potential correction
IDIPOL = 3
LDIPOL = .TRUE.

Au(111):1x1:CO Reference Potential



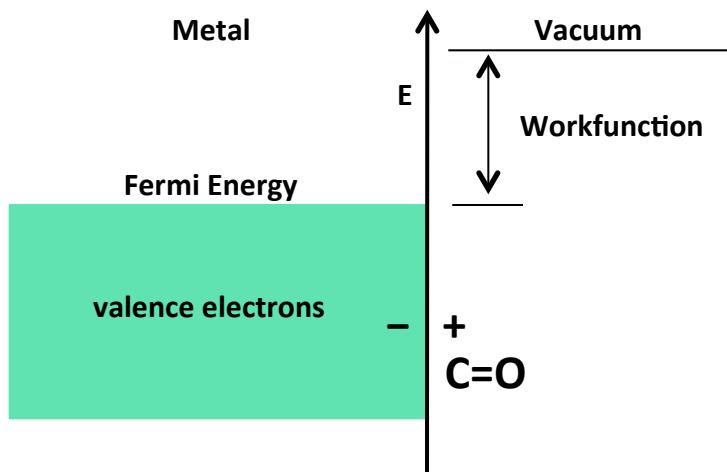
Au(111):1x1:CO Impact on Workfunction

Reference potential from P4Vasp data export, vacuum on CO side, before dipole: 6.278 eV

Fermi energy from OUTCAR: 1.591 eV

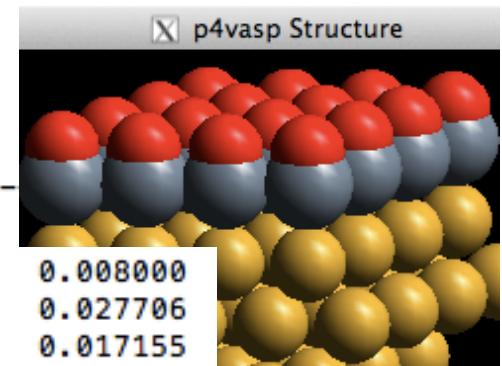
Calculated Workfunction: 4.7 eV
(0.5 eV smaller than clean surface)

Net electron donation from CO lone pair into Au



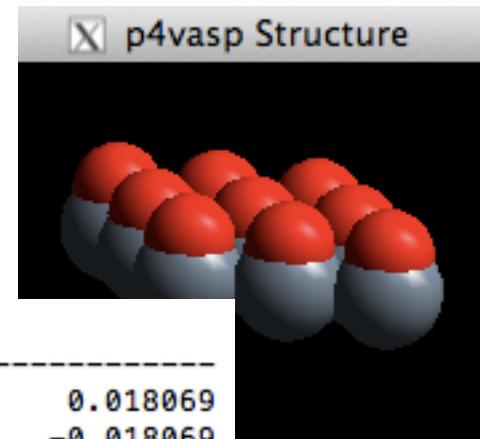
Impact on CO: Compare Reference CO array

| POSITION | | | TOTAL-FORCE (eV/Angst) | | |
|----------|---------|----------|------------------------|----------|----------|
| 0.00000 | 0.00000 | 7.22275 | 0.000000 | 0.000000 | 0.008000 |
| 0.00000 | 0.00000 | 10.16072 | 0.000000 | 0.000000 | 0.027706 |
| 0.00000 | 0.00000 | 11.30484 | 0.000000 | 0.000000 | 0.017155 |



$$d_{\text{Au-C}} = 2.938 \text{ \AA}, d_{\text{C-O}} = 1.144 \text{ \AA}$$

| POSITION | | | TOTAL-FORCE (eV/Angst) | | |
|----------|---------|----------|------------------------|----------|-----------|
| 0.00000 | 0.00000 | 10.16190 | 0.000000 | 0.000000 | 0.018069 |
| 0.00000 | 0.00000 | 11.30366 | 0.000000 | 0.000000 | -0.018069 |



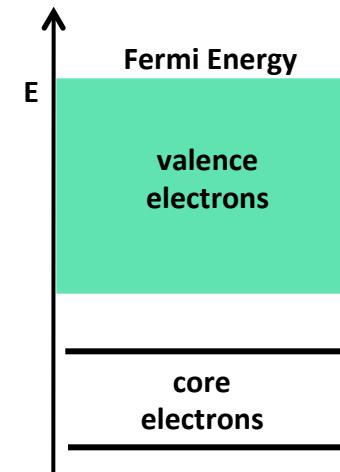
$$d_{\text{C-O}} = 1.142 \text{ \AA}$$

Nota bene: donor-acceptor CO bond to Au – weak bond requires larger basis to converge the binding energy

Core Levels: Initial State Model

Physics:

Reconstruct the core level solutions to the Kohn-Sham equations within the PAW methodology



INCAR

```
ISTART =      1    job : 0-new 1-cont` 2-samecut
ICHARG =      1    Fix charge density from previous CHGCAR
```

Start from previous self-consistent solution

```
Core level calculations: Initial state
ICORELEVEL = 1
```

Request core level calculation

OUTCAR

Example: Au slab with 7 atoms – core levels for each atom

```
the core state eigenenergies are
 1- 1s -80769.3046  2s -14251.9242  2p -12318.7491  3s -3362.7740  3p -2802.1608
          3d -2204.5581  4s -727.5468   4p -543.6810  4d -323.2201  5s -104.7052
          4f -78.3366   5p -55.6345
 2- 1s -80769.5791  2s -14252.2098  2p -12319.0337  3s -3363.0692  3p -2802.4561
          3d -2204.8526  4s -727.8549   4p -543.9905  4d -323.5310  5s -105.0415
          4f -78.6499   5p -55.9748
  . . .
```

Au(111):1x1:CO Example

Raw Data: OUTCAR & P4Vasp potential plots

CO

the core state eigenenergies are

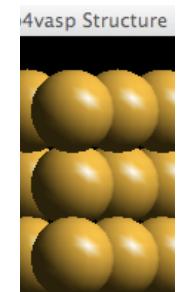
| | | |
|----|----|-----------|
| 1- | 1s | -272.7463 |
| 2- | 1s | -515.1174 |

$$\langle V-\text{Har} \rangle = 0.63 \text{ eV}$$



Au(111) 7 ML

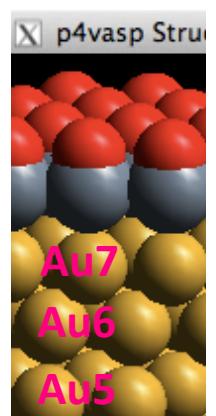
| | | | | | | | | | | |
|----|----|-------------|----|-------------|----|-------------|----|------------|----|------------|
| 5- | 1s | -80769.6854 | 2s | -14252.3175 | 2p | -12319.1412 | 3s | -3363.1769 | 3p | -2802.5637 |
| | 3d | -2204.9603 | 4s | -727.9623 | 4p | -544.0979 | 4d | -323.6385 | 5s | -105.1484 |
| | 4f | -78.7573 | 5p | -56.0808 | | | | | | |
| 6- | 1s | -80769.5791 | 2s | -14252.2098 | 2p | -12319.0337 | 3s | -3363.0692 | 3p | -2802.4561 |
| | 3d | -2204.8526 | 4s | -727.8549 | 4p | -543.9905 | 4d | -323.5310 | 5s | -105.0415 |
| | 4f | -78.6499 | 5p | -55.9748 | | | | | | |
| 7- | 1s | -80769.3046 | 2s | -14251.9242 | 2p | -12318.7491 | 3s | -3362.7740 | 3p | -2802.1608 |
| | 3d | -2204.5581 | 4s | -727.5468 | 4p | -543.6810 | 4d | -323.2201 | 5s | -104.7052 |
| | 4f | -78.3366 | 5p | -55.6345 | | | | | | |



E-fermi : 0.6476 XC(G=0) : -7.7526 alpha+bet : -5.5845 $\langle V-\text{Har} \rangle = 5.85 \text{ eV}$

Au(111) 7 ML + CO

| | | | | | | | | | | |
|----|----|-------------|----|-------------|----|-------------|----|------------|----|------------|
| 5- | 1s | -80768.7414 | 2s | -14251.3733 | 2p | -12318.1971 | 3s | -3362.2319 | 3p | -2801.6187 |
| | 3d | -2204.0154 | 4s | -727.0160 | 4p | -543.1515 | 4d | -322.6919 | 5s | -104.1991 |
| | 4f | -77.8106 | 5p | -55.1305 | | | | | | |
| 6- | 1s | -80768.6482 | 2s | -14251.2787 | 2p | -12318.1025 | 3s | -3362.1394 | 3p | -2801.5263 |
| | 3d | -2203.9226 | 4s | -726.9268 | 4p | -543.0626 | 4d | -322.6032 | 5s | -104.1172 |
| | 4f | -77.7223 | 5p | -55.0519 | | | | | | |
| 7- | 1s | -80768.4647 | 2s | -14251.0868 | 2p | -12317.9115 | 3s | -3361.9397 | 3p | -2801.3265 |
| | 3d | -2203.7235 | 4s | -726.7167 | 4p | -542.8514 | 4d | -322.3909 | 5s | -103.8844 |
| | 4f | -77.5082 | 5p | -54.8156 | | | | | | |
| 8- | 1s | -267.1913 | | | | | | | | |
| 9- | 1s | -509.4840 | | | | | | | | |



E-fermi : 1.5912 XC(G=0) : -8.7964 alpha+bet : -6.3979 $\langle V-\text{Har} \rangle = 6.28 \text{ eV}$

Au(111):1x1:CO Example

Refined Data



| Ref Vac | Au5 5s | Au6 5s | Au7 5s | C 1s | O 1s |
|----------|---------|---------|---------|---------|---------|
| Separate | -111.00 | -110.89 | -110.56 | -273.38 | -515.75 |
| Bonded | -110.48 | -110.40 | -110.16 | -273.47 | -516.76 |

ΔE_{core}

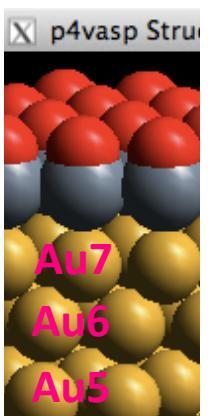
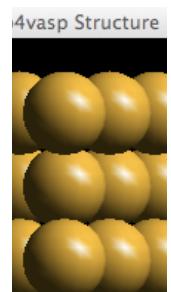
0.48

0.51

0.40

-0.09

-0.01



Note: Change in workfunction is -0.5 eV

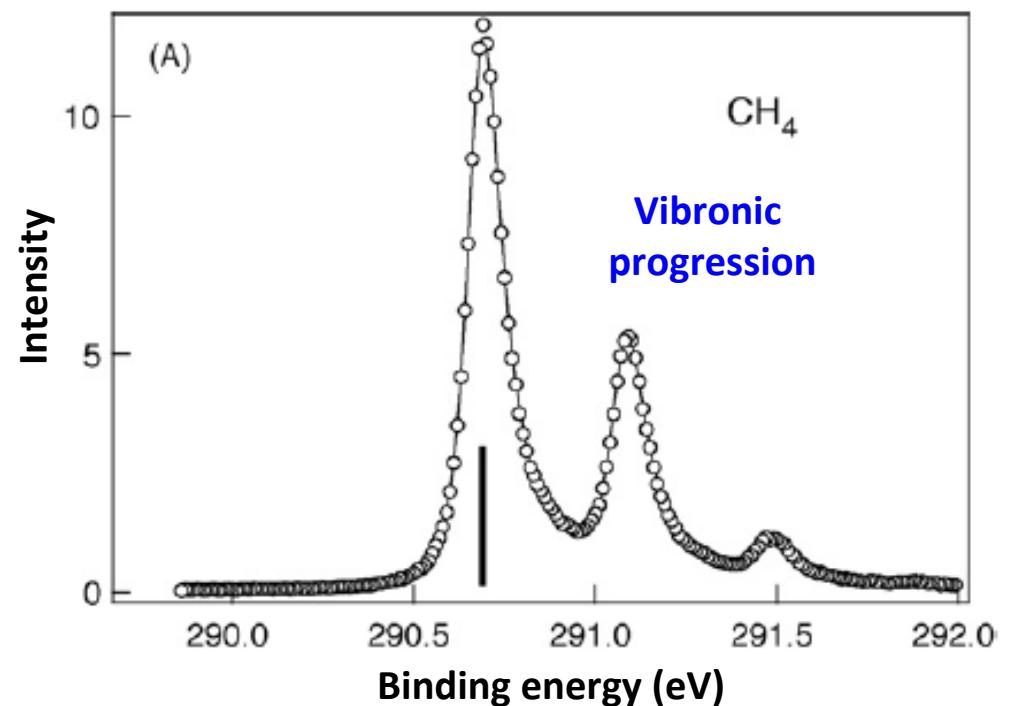
(Verify that Au 5s relative to Efermi for atoms near center of the slab does not change)

Residual small change for Au7 and C, at the interface, reflects local changes in charge – small in this case

Core Level Final State Effects: Molecule Example

| Species | C 1s Binding Energy |
|--------------------------|---------------------------|
| CH_4 | 290.689 |
| CH_3Cl | 292.322 |
| CH_2Cl_2 | 293.783 |
| CHCl_3 | 295.098 |
| CCl_4 | 296.317 |

adiabatic

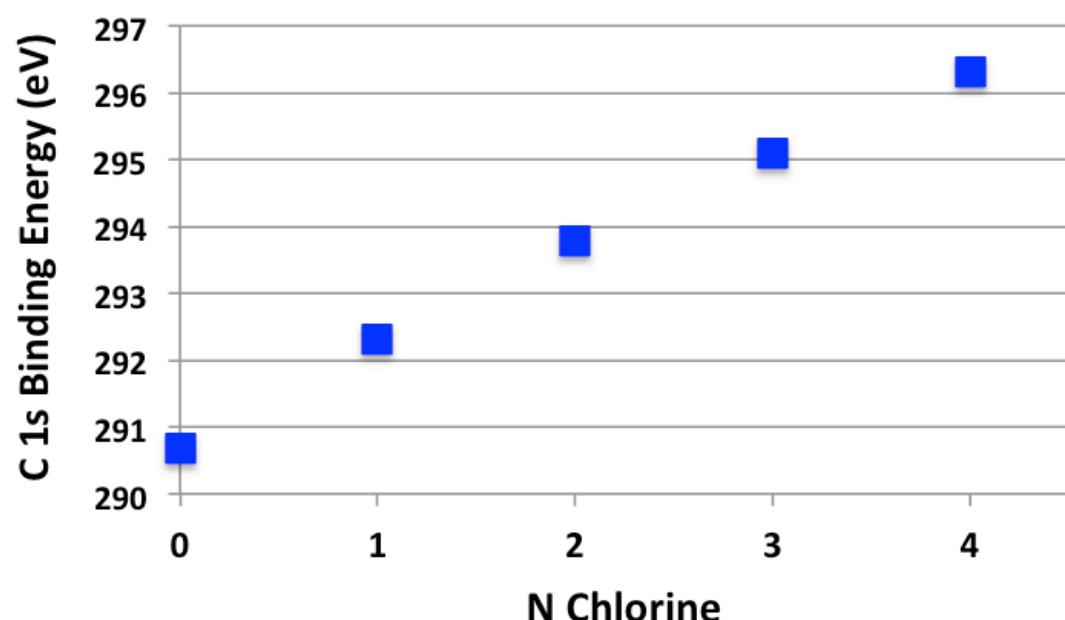


Saethre, Borve, and Thomas, *J. Elec. Spec. Rel. Phen.* **183**, 2, 2011

Core Level Final State Effects: Molecule Example

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adiabatic



Saethre, Borve, and Thomas, *J. Elec. Spec. Rel. Phen.* **183**, 2, 2011

Tutorials: File System – Molecule Example

/software/Workshop14/Tutorials/Tutorial5

Methane

2_1_CH4

2_2_CCl2CH2

2_3_CCl4

CoreInit

CoreFinal

CoreInit

CoreFinal

CoreInit

CoreFinal

To run core levels in lower directories:

> cp CONTCAR CoreInit/POSCAR

> cp CHGCAR CoreInit/.

> cp WAVECAR CoreInit/.

same for CoreFinal

Script for job submission: vpbs.com

Methane Molecule Calculations

INCAR

Initial state model: All core levels at one shot

Core level calculations: Initial state
ICORELEVEL = 1

Final state model: Isolate one atom and one core level

Core level calculations: Final state
ICORELEVEL = 2
CLNT = 1 Atom index
CLN = 1 Core level principle n
CLL = 0 Core level angular l
CLZ = 0.5 Half core charge

Workflow:

Step 1: Molecular relaxation for each case (CH_4 , CCl_2H_2 , CCl_4)

Step 2: Initial state calculation (using CONTCAR, CHGCAR, WAVECAR)

Step 3: Final state calculation (ditto)

**For 2 & 3, Average potential analysis to find value near mid-box as a reference
(Note dipole in the CCl_2H_2 case: overlook the small field – approximation)**

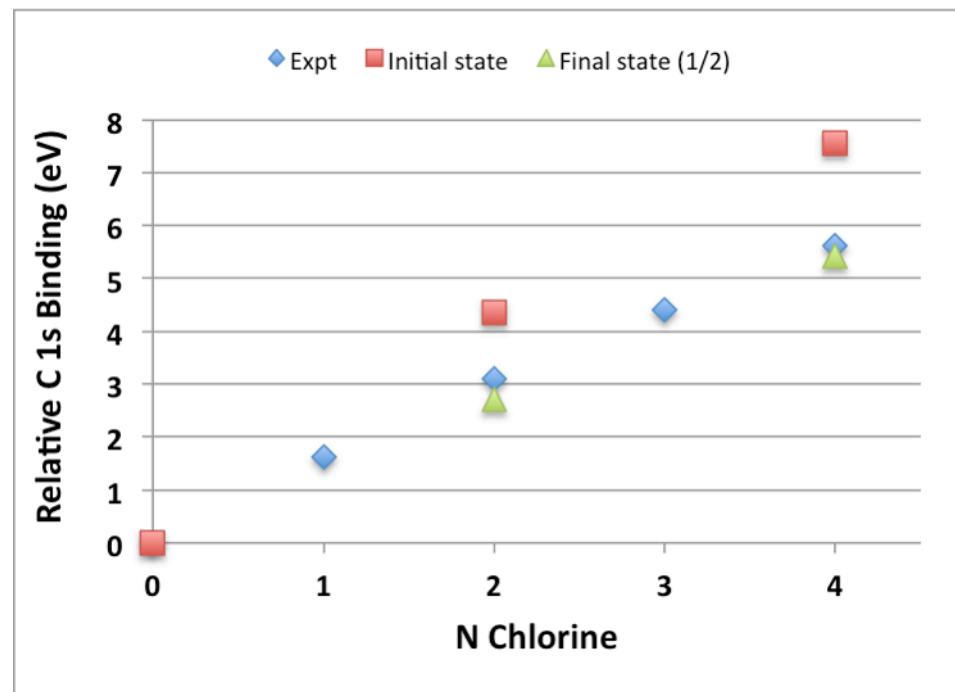
Molecular Example: Results

Raw data

| Species | Initial | | Final | |
|---------------------------------|---------|----------------------------------|---------|----------------------------------|
| | C 1s | $\langle V_{\text{Har}} \rangle$ | C 1s | $\langle V_{\text{Har}} \rangle$ |
| CH ₄ | -268.60 | 0.03 | -295.54 | 0.06 |
| CCl ₂ H ₂ | -272.87 | 0.12 | -298.05 | 0.12 |
| CCl ₄ | -275.97 | 0.20 | -300.82 | 0.20 |

Relative core level binding energy shifts:
Rationalize final state effect

First person to explain the error in this example to Hybertsen gets a free drink tonight



Final States Approach: Comments

VASP approach: Create a core hole and inject the electron back into the empty states

- This is more analogous to the X-ray absorption situation than the photoemission scenario which leaves a charged system
- Other approaches deal with a charged final state

VASP offers a continuous choice in whether a full core hole or a partial core hole is created

- The choice $\frac{1}{2}$ is used here and widely advocated by some groups (e.g. Pettersson)
- Other groups prefer a full core-hole
- Empirical testing is recommended

Extensions for Self Study

To perform these exercises, you will need to adapt the input files you already have.

Return to the Au(111):1x1:CO example. Put in the flags necessary to calculate the projected DOS. Analyze the pDOS to understand the sigma donation / pi back donation.

- See tutorials 3_2 and 3_7 from Tutorial 2 for more details

Return to the clean and CO covered Ni(111) (3_4, 3_5) from Monday, Tutorial 1 and repeat the initial state core level shift analysis, following the pattern from the Au(111) example here.

- Are the shifts on the C 1s level similar, larger? Why?